Removal of some heavy metals from aqueous solutions using natural wastes orange peel activated carbon

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ABSTRACT

The adsorption of heavy metals by various types of activated carbon originated from natural wastes is an effective, low-cost and innovative method for their removal from aquatic environments. This study aims to determine the applicability of adsorption isotherms models during the adsorbent activity of orange peel activated carbon for removal of Pb^{+2}, Ni^{+2}, Cr^{+3} and Cd^{+2} ions. The specific surface area, micropore area, and the effects of pH value, soaking time and dosage of orange peel activated carbon were investigated in this study. The optimum pH values for adsorption capacity and removal efficiency of heavy metal ions were 5 – 6. The optimum soaking time was 120 min for Pb^{+2}, 210 min for Ni^{+2} and Cr^{+3} and 240 min for Cd^{+2}. The optimum adsorbent dosage for removal of the studied was 2 gm. The isotherm equilibrium studies confirmed that both Langmuir and Freundlich adsorption isotherms well fitted models and revealed that adsorption of metals ions is one layer adsorption and confirmed highly efficient orange peel activated carbon in the removal of heavy metals. The environmentally friendly origin of orange peel indicates that could use in many broad-scale, low cost-effective and alternative applications.

Key words: orange peel; Activated carbon; Adsorption capacity; Removal efficiency; Heavy metal ions

INTRODUCTION

Heavy metals removal from its aqueous solutions attracted the attention of many scientific communities, especially from industrial and domestic wastewater, as the quest for green chemistry takes centre stage. Heavy metals causes serious hazardous to the environment and therefore their removal from wastewater before discharging into current waters is a great important issues (Marin et al., 2009). These substances are stable and persistent environmental contaminants since they are non-biodegradable (Sud et al., 2008).

Cadmium, chromium, copper, lead, mercury, nickel and arsenic cause a serious case of pollution to the human body (WHO, 2004). Lead and chromium ions Concentrations of 0.005 mg/l , 0.001 mg/l for Cd^{2+}, Ni^{2+} and As^{5+} and 0.1 mg/l for Cu^{2+}, will fatal and cause illness in humans (Kawarada et al., 2005).

The removal of heavy metal ions is an important problem in the field of water purification. Recently, activated carbon from different origin natural waste or crude materials is one of the materials has been widely used to remove metal ions from aqueous solutions (Issabayeva et al., 2006). The increasing variety and amounts of potentially hazardous impurities in water have led to the increased use of activated carbon (Ali et al., 2016).

Adsorption of heavy metals on surface of activated carbon materials is one of the more popular methods for the removal of metals ions from the aqueous solutions. Whereas, the adsorption is a surface phenomenon, in which molecules of adsorbate (metals ions) are attracted and held to the surface of an adsorbent (activated carbon materials) until an equilibrium is attained between adsorbed molecules and those still freely distributed in the carrying gas or liquid (Rađenoviæ et al., 2011).

The solution pH value was greatly affected the metal ion adsorption, which concerns the solubility of metal ions, ion concentration of adsorbent functional groups, and degree of ionization of the adsorbate in the reaction. The surface chargeof the adsorbent could be improved by changing the solution pH value (Saifuddin and Kumaran, 2005).

The application of orange peel as a biosorbent material presents strong potential due to its main components of cellulose, pectin, hemicellulose and lignin which contain functional groups as possible binding sites for metals (Kaushik et al., 2009). Orange peel is an attractive and economic alternative for the removal of metal ions from waste water (Acar et al., 2015; Tran et al., 2016; Abid et al., 2016).

The aim of this work was to study the adsorption capacity of orange peel for removing some heavy metals (Pb, Ni, Cr, Cd) ions from aqueous solutions, also to investigate effects of contact time, initial metal ion concentration, pH and biosorbent dosage on the biosorption efficiency.

2. MATERIALS AND METHODS

2.1. Adsorbent preparation*:*

Orange peel obtained from agricultural wastes of orange fruit. The fruits were first peeled off to obtain the outer skin of the fruits the peel was washed with ordinary tap water to remove possible foreign materials present (dirt and sands). Washed samples material were dried at 80 ^{0}C in electrical oven overnight and then crushed with a mortar and pestle to reduce the size. 250 gm of the small pieces was carbonized at 400°C for 15mins and then subsequently activated using 1.0 M $ZnCl_2$ at 500 ^{o}C for 2-3 hours. The activated materials were allowed to cool naturally inside the furnace to room temperature before they were removed for analysis. The activated carbon from orange peel was pulverized to a geometric mean particle size of 180–150 μm and stored at room temperature.

2.2. Adsorbent characterization

The BET (Brunaeur–Emmet–Teller) multipoint method (Jankowska et al., 1991) and Langmuir method (Gregg and Sing, 1982) were used to determine the surface area. Nitrogen (N_2) gas was used to determine the adsorption isotherms (Lowell and Shields, 1991). The micropore volume and micropore area of produced activated carbon was measured using the t-plot method (De Boer et al., 1966; Sing et al., 1985). Scanning electron microscopy (SEM) analysis was carried out on the orange peel carbon samples, to study its surface morphology using JSM-5600model scanning electron microscope. SEM has a high resolution, making higher magnification possible for closely spaced materials. Carbonaceous materials of orange peel was characterized by diffuse Fourier-transform infrared analysis (FTIR) to qualitatively determine the functional groups in frequency ranged between 4000 to 400 cm^{-1} using spectrometer (Thermo Nicolet, NEXUS, USA) at room temperature..

2.3. Adsorption capacity and removal efficiency of heavy metal ions

Different serial standard solutions of lead, Nickel, chromium and cadmium were prepared from stock solution (1000 mg/L) of each metal. The adsorption of different metals on orange peel carbon adsorbent was studied by batch method. The activated carbon was first placed in a 250-ml Erlenmeyer flask. 20 ml of a standard heavy metal solution was added to the flask. The mixtures were stirred continuously for 2 hr, and then the samples were centrifuged for 5 minutes at 5000 rpm and the supernatant of each sample was analyzed using ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy; Spectro Genesis, Germany). The adsorption capacity of heavy metal ions by activated carbons could be expressed as follows (Horsfall et al., 2006; Zulkali et al. 2006):

$$q_{e}=\frac{(C_0-C_e)\ x\ V}{M}$$

$$R\ \%=\frac{(C_0-C_e)\ x\ 100}{C_0}$$

Where; C_0 is the initial metal ions concentration, C_e is the concentration of metal ions in solution (mg/L) at equilibrium, C_t is the concentration of metal ions in solution (mg/L) at time, t in solution, V is volume of initial metal ions solution used (L) and M is mass of adsorbent used (g).

3. RESULTS AND DISCUSSION

3.1. FT-IR analysis of adsorbent

FTIR spectroscopy technique was used to show the functional groups present on the surface of the peels. Figure 1 shows FTIR spectra of the orange peel. On the peels surface there are many functional groups were presented, the OH groups appear around the peak of 3450 cm^{-1}, free OH groups and bonded OH bands of carboxyl group were observed as the OH stretching vibrations (Marín et al., 2010). The peak of CH stretching vibrations of CH, CH_2, and CH_3 groups was appeared at 2925 cm^{-1} (Kamsonlian et al., 2011). The asymmetric and symmetric stretching vibrations of the C-O groups appeared at peaks around 1760 and 1620 cm^{-1} respectively. Furthermore, peaks at 1060 cm^{-1} is due to stretching vibration of C–OH of alcohols and carboxylic acids (Liang et al., 2009; Goher et al., 2016).

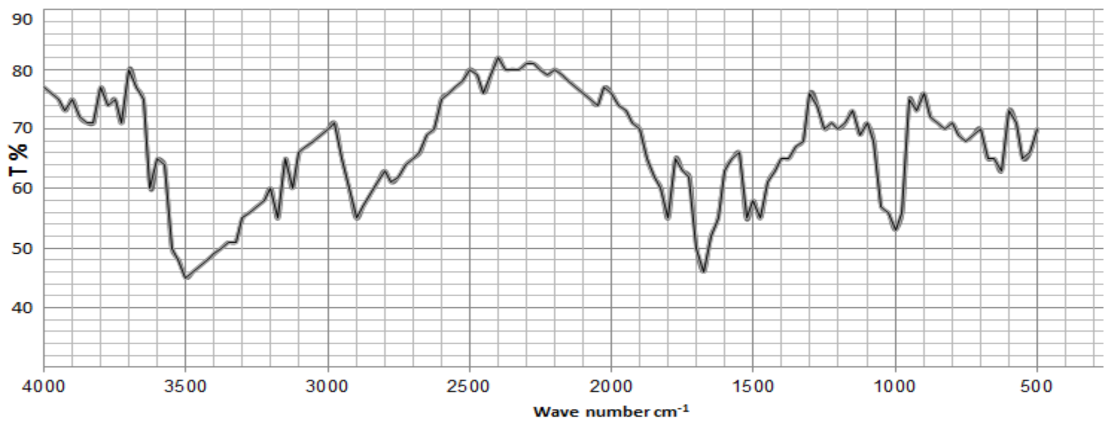

Fig. 1. FT-IR spectrum of chemically modified orange peel

The images of Scanning Electron Microscope of activated carbon produced from orange peel (Fig. 2) shows that wide varieties of morphological structure in the activated carbon before and after metal's sorption, the surface have a smooth pores with definite dimension before adsorption. After biosorption, some morphological changes have been occurred due to the exposure of heavy metal (Annadurai et al., 2003; Bernard and Jimoh, 2013).

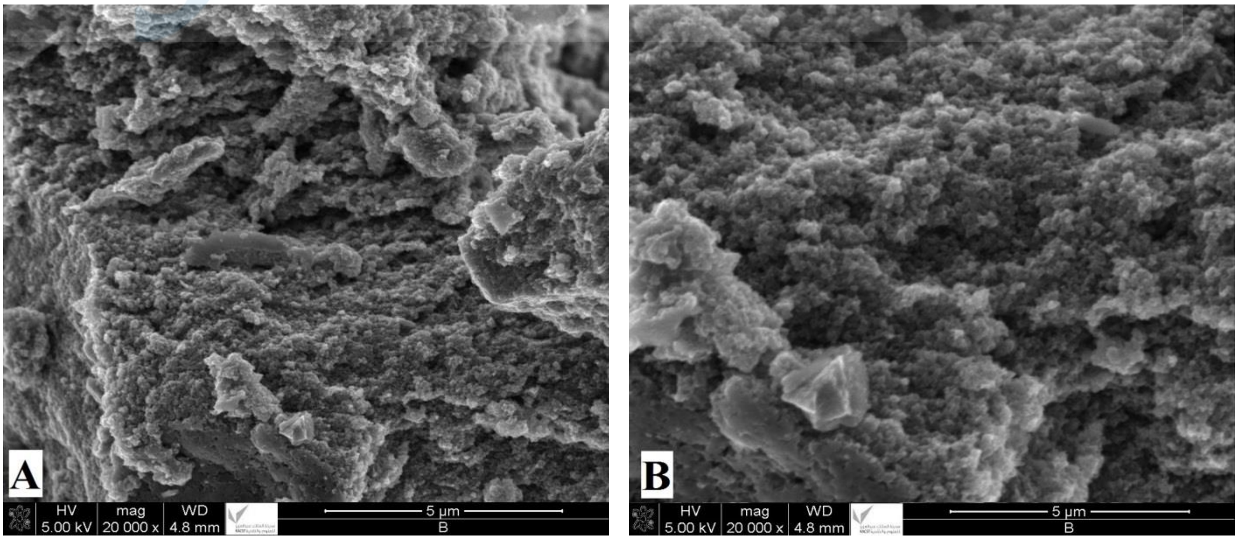

Fig. 2. SEM micrograph of orange peel (A) before and (B) after metals sorption

3.2. Surface area analysis

Some of the physical properties of the orange peel activated carbon which were determined by BET method were shown in table (1). The N_2 adsorption gave the specific surface area (S_{BET}) of 1.4 m^2/g which is close to other values reported in some literature for orange peels (Khalfaoui et al., 2014) who reported a 1.6 to 2.3 m^2/g for different modified orange peel absorbents.

Table 1. Physical properties of orange peel

Property	Magnitude
Surface area (m^2g^{-1})	1.40
Total pore volume (cm^3g^{-1})	0.000206
Pore diameter (Å)	20.61

3.3. Effect of pH on adsorption of heavy metals

The pH is one of the imperative factors governing the adsorption of the metal ions which affects of the functional groups protonation and also, the metal chemistry (Lo et al., 2012). Figure 3 showed the removal of aqueous solution of Pb^{+2}, Ni^{+2}, Cr^{+3} and Cd^{+2} at varying pH range from 3 to 9 under the precise conditions (initial metals concentrations 10 mg/l, at constant contact time of 250 min, with 1 g of the adsorbents used, and at a room temperature of 28 ^{o}C). It obvious from the results the removal of studied ions increased markedly with low pH values. The maximum adsorption of Pb^{+2} ions was observed at pH ranged between 5.5 to 6 with removal efficiency ratio reached to 80%, then the efficiency gradually decrease by increasing pH values (Fig. 3). At pH 5, maximum removal was obtained for Ni^{+2} and Cd^{+2} ions, with 78 and 77.2 % removal efficiency, respectively. While 89.6% removal efficiency of Cr^{+3} ions was achieved even at a low pH of 4. The obtained results were agreement with those obtained by Kadirvelu et al. (2000) and Kobya et al. (2005) who found that the maximum removal efficiency of Pb^{2+} (100%), Cd^{2+} (100%) occurred at a pH value of 4–5 by activated carbon, while Cr^{+3} (98.56%) at pH of 4 and for Ni^{2+} (97.59%) at pH value of 4.

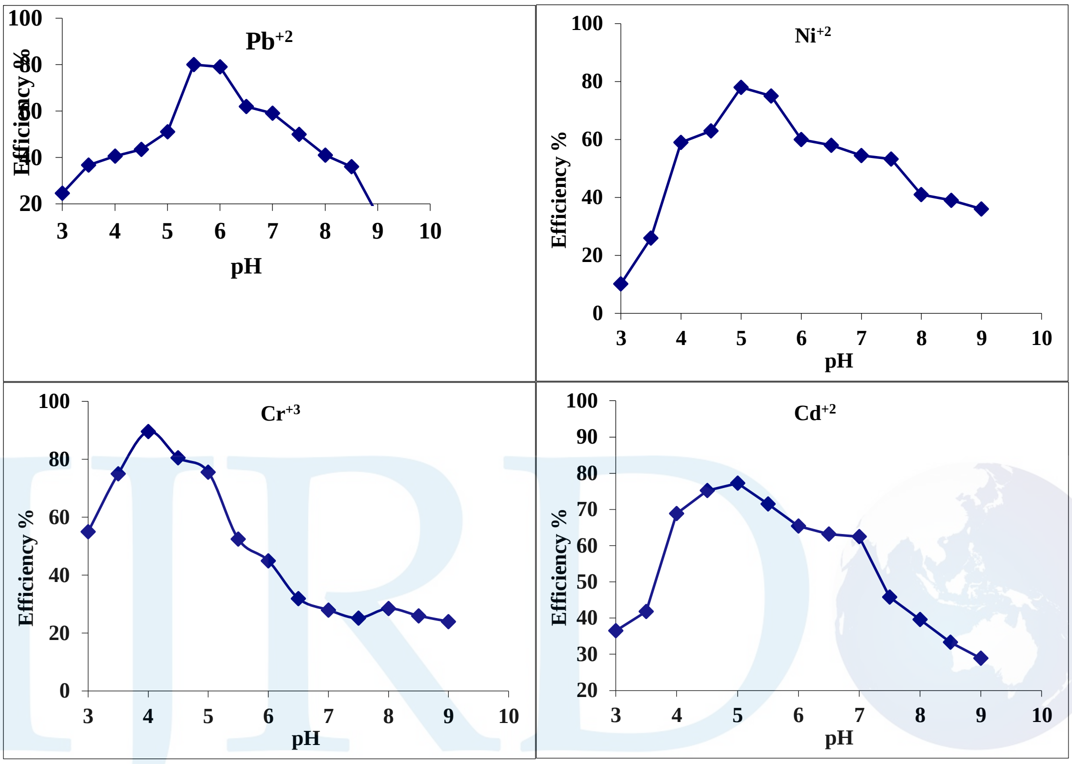

Fig. 3. Effect of pH on removal of metals Pb^{+2}, Ni^{+2}, Cr^{+3} and Cd^{+2} by orange peel, initial metal concentration 10 mg/L

3.4. Effect of contact time on adsorption of heavy metals

Figure 4 illustrates the effects of soaking time on removal capacity of heavy metal ions using 0.5 g of the orange peel activated carbons at room temperature 28 ^{0}C for fixed intervals of 20 min. the obtained results reveal that the metal ions removal efficiency were increased as increases of contact time This is due to prolonged contact between the sorbent surface and the metals ions (Bernard et al., 2013).

The percentage metal ions removal approached equilibrium within 120 min for Pb^{+2} with maximum removal efficiency reached to 96%, while for Ni^{+2} and Cr^{+3} recorded 210 min with removal efficiency of 80.2 and 91.3 % respectively. Furthermore, removal approached equilibrium of Cd^{+2} within 240min with removal efficiency of 91.2 %. Having an decreasing order trend of Pb^{2+}>Cr^{3+}>Cd^{2+}>Ni^{2+}, after which further increase in time did not affect the removal efficiency about any further improvement for the metal ions, but resulted in desorption of some of the metal ions (Cr and Cd) from the adsorbent surface occurred (Moghadam et al., 2013)

From figure 4 it was clearly that, the rate of adsorption is higher within the first 120 min due to large available surface area of the adsorbent and a high concentration gradient. By time is passed, exhaustion of adsorbent's active sites will be happened thus attained the equilibrium, further the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles (Verma et al., 2006).

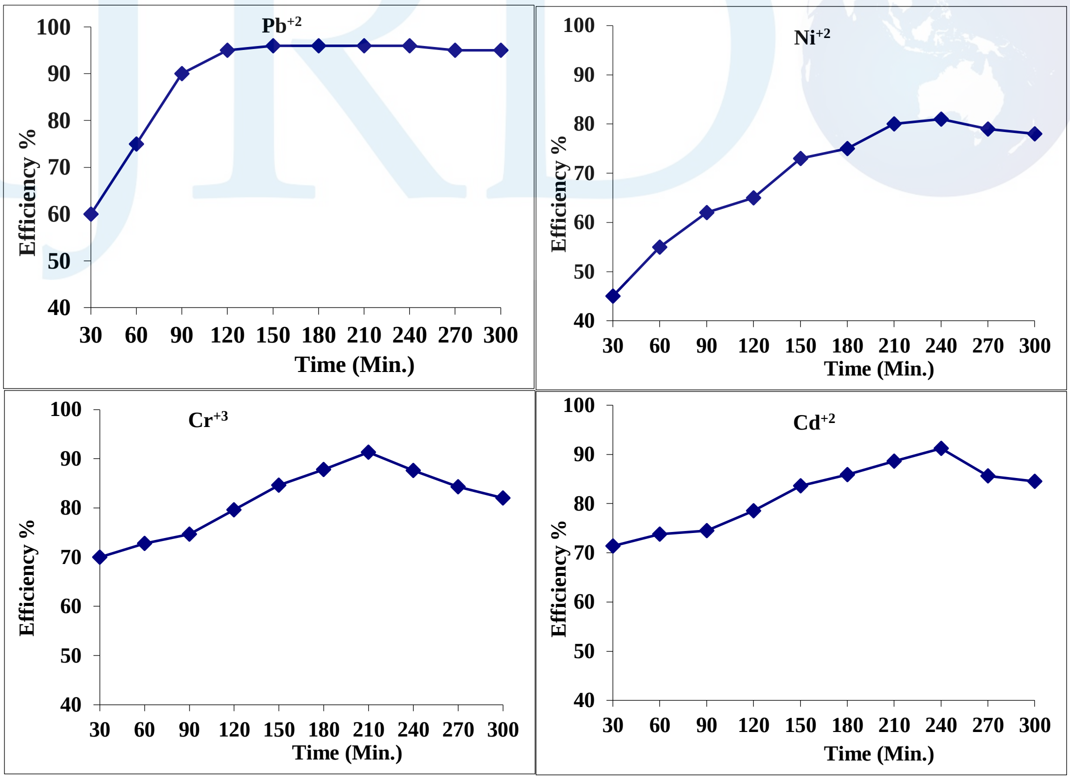

Fig. 4. Effect of contact time on removal of metals Pb^{+2}, Ni^{+2}, Cr^{+3} and Cd^{+2} by orange peel, initial metal concentration 10 mg/L

3.5. Effect of adsorbent dosage on adsorption of heavy metals

The effect of adsorbents concentration considered as one of the most strongly parameters that affects the removal efficiency and adsorption capacity among other studied parameters. Figure 5 shows the effect of the different adsorbents dosages (0.5-2 g/100ml) on different metals concentrations (1, 10, 20 and 40 ppm) solution for 2 hours at room temperature 28 ^{0}C. The adsorption capacity of Pb^{2+}, Ni^{2+}, Cr^{3+}, and Cd^{2+} increased with increasing the metals ions concentrations and dosage of orange peel activated carbons. The removal of Pb^{+2} and Ni^{+2} attained maximum removal, even at a lower adsorbent dosage with 99% and 91.6 % removal for 2 g/100 ml adsorbent and 40 ppm metals concentration respectively. On the other hand, removal efficiency of Cr^{+3} and Cd^{+2} show narrow variation with increasing of metal concentrations, but it increase with increasing of adsorbent dosage increase in adsorbent dosage (Fig. 5). Maximum removal of Cr^{+3} 85.2 %was attained at 2 gm adsorbent with 40 ppm metal ions concentrations. Hence 2 gm was chosen as the optimum adsorbent dosage for removal of the studied. Higher dosage of adsorbent increased the adsorption due to more surfaces and functional groups been available on the adsorbent (Esposito *et al*., 2001).

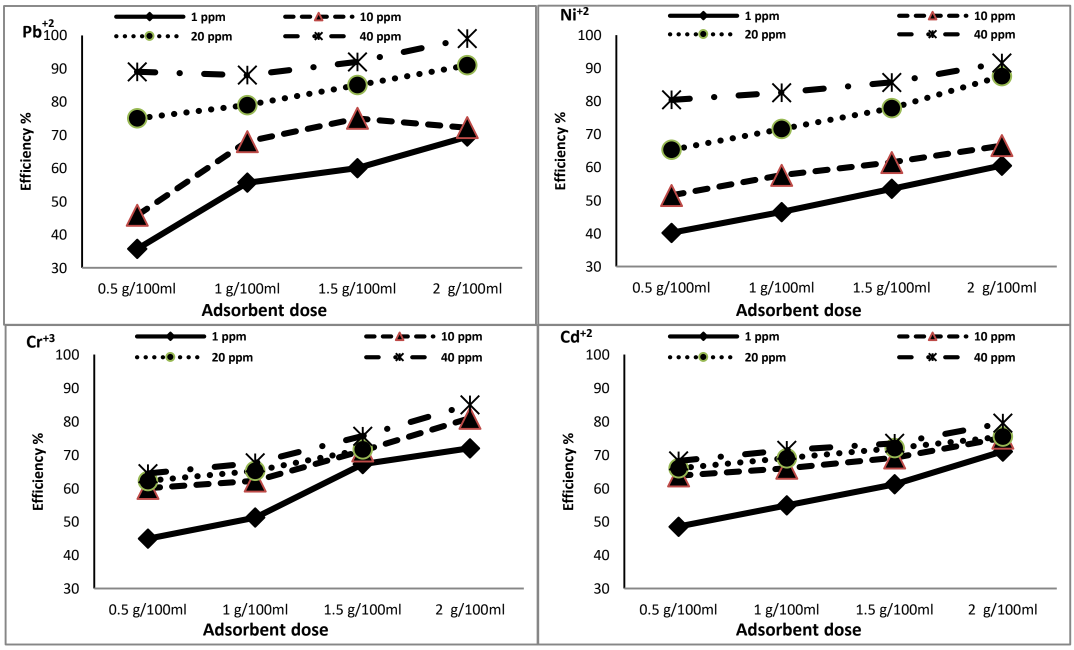

Fig. 5. Effect of adsorbent dosage on removal of metals Pb^{+2}, Ni^{+2}, Cr^{+3} and Cd^{+2} by orange peel, initial metal concentration 1, 10, 20 and 40 mg/L

3.6. Adsorption isotherms

The equilibrium adsorption of Pb, Ni, Cr and Cr ions were studied at optimum conditions (pH =6.0) and agitation time (40 min) at different concentrations ranging from 1 to 10 mg/l and 0.5 to 2 g/100ml for ions and adsorbent, respectively) and modeled using adsorption isotherm of two well-known isotherm models for the single solute systems, i.e., Langmuir and Freundlich. The adsorption isotherm can be used to optimizing the use of adsorbent through describing how the solute interacts with the adsorbent (Moreno-Piraján and Giraldo, 2012).

3.6.1. Langmuir isotherm

As a first theoretical models assumes that adsorption will occurs at specific homogenous active sites of the sorbent is Langmuir isotherm (Moghadam et al., 2013). This model, which is used successfully in many monolayer biosorption processes, is given by the equation:

$$q_e = \frac{q_m\, K_L C_e}{1 + K_L\, C_e}$$

Where: q_m (mg g^{-1}) the monolayer adsorption capacity

K_L (L mg^{-1}), Langmuir constant

q_e (mg g^{-1}), the amount of metal ion adsorbed per 1 gram of the adsorbent at equilibrium; and

C_e g L^{-1} the equilibrium metal ion concentration

The plotted graph between C_e/q_e versus the C_e which gives a straight line of slope ($1/q_m$) and intercept ($1/K_L{*}\, q_m$), q_m and K_L can be determined. As shown in figure 6, R^2

values for Cd^{+2}, Ni^{+2} and Pb^{+2} are greater than 0.90 which indicate that the adsorption of these ions onto orange peel activated carbon follows the Langmuir model, while Cr^{+3} have R^2 value of 0.79 that means this adsorption don't obey Langmuir isotherm model.

The adsorption efficiency for the studied metals ions in Langmuir isotherm follows the order of $Cd^{+2} > Ni^{+2} > Pb^{+2} > Cr^{+3}$. These data were agreement with that obtained by Ali et al., (2016) for removal Pb, Cd, Cu using died cells of *Chlorella vulgaris*

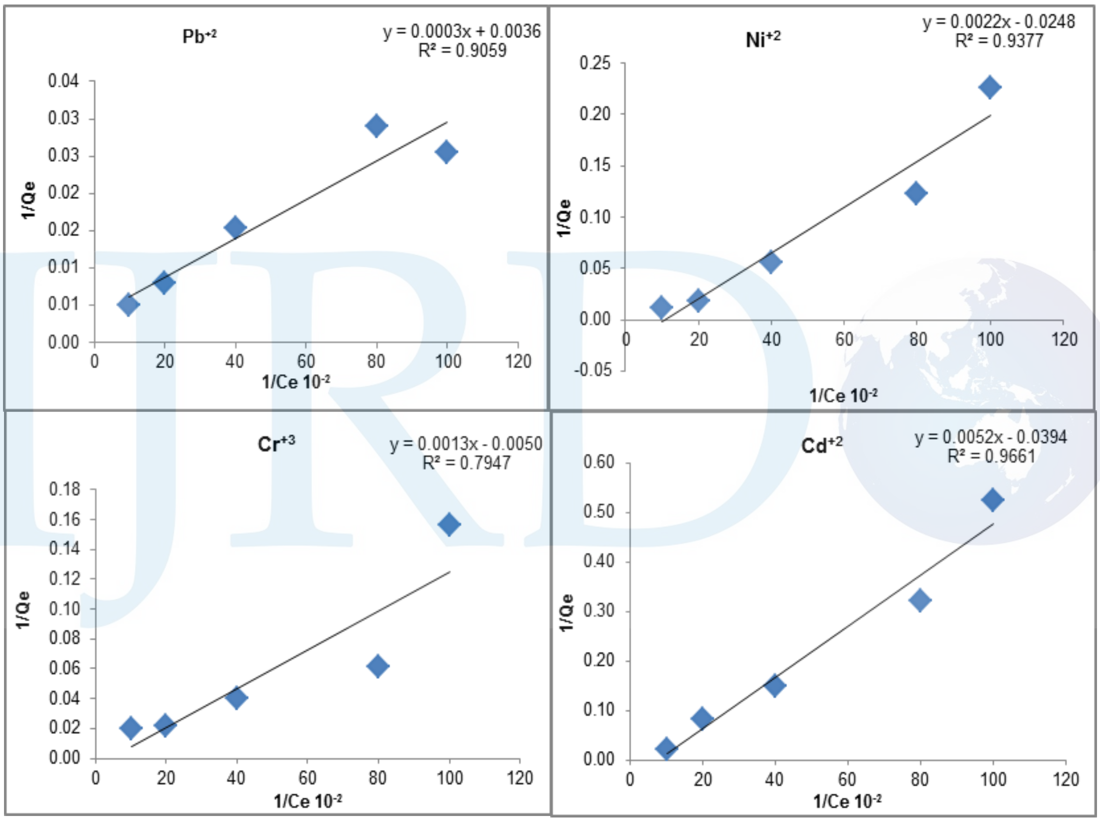

Fig. 6. Langmuir isotherm plot for adsorption of lead, Nickel, chromium and cadmium ions by orange peel active carbon

3.6.2. Freundlich isotherm

This model is based on sorption of heterogeneous energetic active sites distribution accompanied by interactions between adsorbed molecules. This isotherm is derived from the assumption that adsorption sites are distributed exponentially with respect to the heat of adsorption. The model is described by the following equation

$$q_e = K_f C_e^{1/n}$$

The logarithmic form of the Freundlich equation yields a linear plot with respect to the relation between log q_e versus log C_e:

$$\log q_e = \log K_f + 1/n \log C_e.$$

Where: q_e is the amount of metal adsorbed by orange peel biomass (mg/g), C_e is the equilibrium adsorbate concentration in mg/L, K_f is the adsorbent capacity measure and n is the adsorption intensity that can be determined from the linear plot

The linear Freundlich isotherm graphs are presented in figure 7. Values of the correlation coefficients show that the Freundlich isotherm is convenient appropriate to characterize for the adsorption of the all studied metals ions onto orange peel active carbon, with R^2 = 0.9991, 0.9962, 0.9852 and 0.9682 for Cd^{+2}, Pb^{+2}, Ni^{+2} and Cr^{+3} ions respectively. The R^2 values of the Freundlich isotherm is greater than obtained by Langmuir isotherm, indicating applicability of this model more better than Langmuir one especially for Cr^{+3} ions. The adsorption efficiency for the studied metals ions in Langmuir isotherm follows the order of $Pb^{+2} > Cd^{+2} > Ni^{+2} > Cr^{+3}$

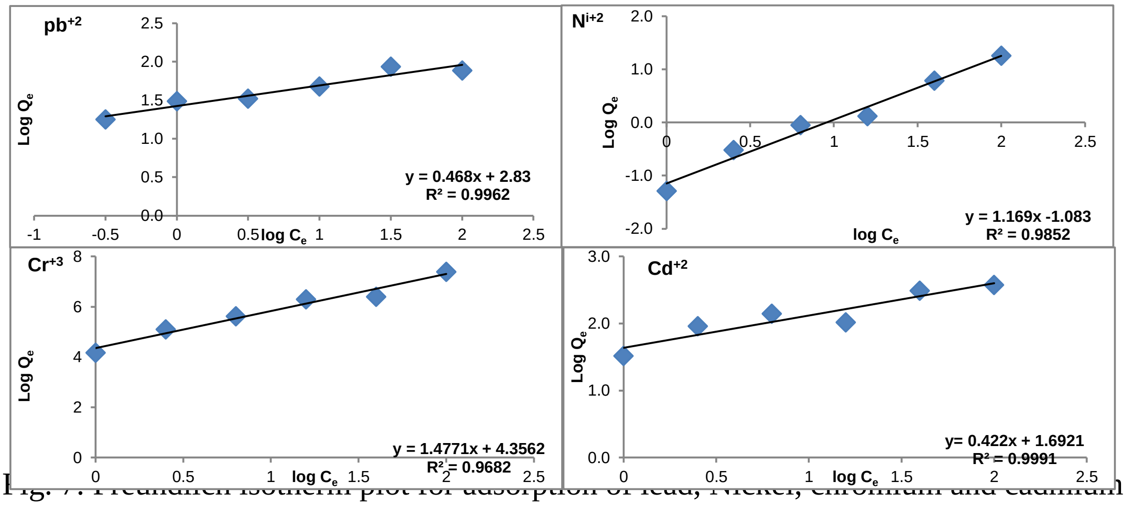

Fig. 7: Freundlich isotherm plot for adsorption of lead, Nickel, chromium and cadmium ions by orange peel active carbon

4. **CONCLUSION**

In this study, orange peel activated carbon adsorbent was used successfully for the adsorption of Pb^{+2}, Ni^{+2}, Cr^{+3} and Cd^{+2} metals ions from their aqueous solution. The obtained results revealed that the adsorption of metals ions is time dependent, pH dependent and adsorbent dosage dependent. Orange peel is inexpensive natural waste and readily available, thus this study provide a low cost effective means for removing metal ions from contaminated water or effluents. The isotherm equilibrium studies confirmed that both Langmuir and Freundlich adsorption isotherms show that adsorption of metals ions on orange peel activated carbon is one layer adsorption.

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